TITLE: **COAL AND COAL CONSTITUENTS STUDIED BY ADVANCED EMR TECHNIQUES**

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ABSTRACT

Advanced electronic magnetic resonance (EMR - also called electron paramagnetic resonance, EPR, or electron spin resonance, ESR) methods are used to examine properties of coals, chars, and molecular species related to constituents of coal. EMR methods can be used to probe such materials because they typically contain a high concentration of unpaired electrons whose spin magnetic moments interact with the surrounding structure and provide convenient spectroscopic reporters of that structure.

An important and unique EMR method for analytical and structural examination of coal and related materials is high-frequency (HF) EMR. At high frequencies, resolution and analytical specificity are greatly enhanced. The necessary facilities and experience for HF-EMR and for its application to study carbonaceous materials are available in only a very few laboratories around the world, including this one. Here we have set up a 100 GHZ general-purpose HF-EMR spectrometer adaptable for a wide range of experiments. Sample results for coals and coal constituents are shown in this presentation.

An early task of this project has been to progress toward completing a second 100-GHZ HF-EMR system that would be special-purpose – especially suitable for the study of organic radicals such as those found in coals and related materials -- and that would be available for the DOE project work and similar studies even when the general-purpose system is preempted for other kinds of studies. Features of this system are reported.

The analytical use of HF-EMR spectroscopy would be greatly facilitated if it could be informed by a predictive theory relating the EMR spectral parameters to structures of the aromatic radical species. This group has put some effort into adapting quantum mechanical theories for this purpose and has achieved some success in applications to oxygen- and sulfur-containing aromatic species.

The interactions of water with coal are important factors in all aspects of coal cleaning and utilization. It has long been suspected that water adsorbed in the pores of the coal matrix effects the EMR spectral line shapes seen by advanced Electron Magnetic Resonance (EMR) methods. Recently, we developed a very-low-field, low-frequency, pulsed dynamic nuclear polarization (DNP) spectrometer capable of observing the interactions of water with the surfaces of carbonaceous solids. In these DNP experiments, radiofrequency pulses excite electron spin transitions in carbonaceous particles suspended in water or other fluid medium in a magnetic field, the magnetic polarization is transferred to protons in the medium by interaction between surface electrons and medium, and proton spin echoes are used to detect the NMR enhancement resulting from this polarization transfer and to follow the relaxation behavior of the electronic spin system in the particles.

Experiments with this novel DNP instrument examined different kinds of carbonaceous particles. Both negative enhancements, indicating dipole-dipole (through-space) interactions between carbonaceous particle surface and liquid, and negative enhancements, implying an intimate contact between surface and the molecules of the liquid, have been found. Recently, we explored an approach to characterize carbonaceous microparticulates based on the correlation between porous structure parameters, determined by classical adsorption data, with information obtained by advanced magnetic resonance and other techniques. The combined results, interpreted in terms of thermodynamic and dynamic models of the interaction processes, suggest some new insights that this approach may provide for coal research.